*Research article*

# Study on the fabrication and investigation of the structural, optical and photocatalytic properties of $Co^{2+}$, $Ni^{2+}$ co-doped ZnO nanomaterials

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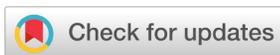
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**ABSTRACT**

In this study, $Co^{2+}$, $Ni^{2+}$ co-doped ZnO nanomaterials (Co,Ni-ZnO NMs) were successfully fabricated by hydrothermal method at low temperature at 90°C for 12 hours. $Co^{2+}$ and $Ni^{2+}$ ions were doped into the ZnO nanomaterials at ratios of 1 mol% and 2 mol%, respectively (calculated compared to the number of moles of $Zn^{2+}$). The methods used to study on the structure and properties of materials such as XRD, SEM/ EDX and UV-vis spectra. The results showed that the fabricated materials were in the form of wurtzite single-phase and nanometer structure. The optical band gap energy (Eg) of Co, Ni-ZnO NMs was determined based on to the Kubelka–Munk equation and achieved a the value of 3.17 eV. The Eg of undoped ZnO was about of 3.34 eV. Reducing this optical gap energy of the material is desirable in research on semiconductor materials with the aim to improve the applicability of materials that are responsive under irradiation of light shifted to visible region. Besides, the results also showed that the ZnO nanomaterials co-doped with $Co^{2+}$ and $Ni^{2+}$ achieved a photocatalytic efficiency for degradation of the methylene blue (MB) dye solution in the visible light regions. Thus, ZnO material co-doped with $Co^{2+}$ and $Ni^{2+}$ ions has achieved superiority in optical applications stimulated by visible light (undoped ZnO material only achieves optical applications in the ultraviolet light region). The rate constant for the MB dye photocatalytic decomposition reaction had been determined according to the Langmuir Hinshelwood (L-H) kinetic model. This decomposition rate constant of the fabricated samples all complied with the first-order kinetic model with a high $R^2$ correlation coefficient (achieved above of 0.92). The rate constant of the Co,Ni-ZnO NMs sample was approximately 17.8 times larger than that of the undoped ZnO sample (achieved 0.006204 and 0.0003471 $min^{-1}$, respectively).

**Key words:** Wurtzite ZnO nanostructure, Co2+, Ni2+ co-doped ZnO, Kubelka–Munk, visible light irradiation

## INTRODUCTION

The environmental pollution, especially water pollution, is a global issue. Organic dyes are one of the pollutants that have durability and high temperature stability, colorant, potentially carcinogenic and toxic. These pollutants release into the environment lead to health, aesthetical and serious environmental threats. Therefore, their removal from the industrial wastewater sources is a very necessary[1–7]. Currently, in applied research to treat organic dyes in wastewater, attention is often paid to using two main types of materials: adsorbent and photocatalytic materials[8–12]. In addition, the ZnO semiconductor is also a good photocatalytic material for environmental treatment. ZnO nanostructured material is characterized as a group II-IV semiconductor with a wide optical gap (3.37 eV) and large excitation binding energy (60 meV)[13–17]. ZnO nanomaterials also have the advantages of having many diverse shapes such as nanorods, nanowires, nanofibers, nanospheres, nanosheets, nanosheets, nanoscales, nanotubes, flower shape,...[18–22]. Materials fabricated methods are also very diverse such as sol-gel, hydrothermal, wet chemistry, hydrothermal ultrasound, co-precipitation,...[23–31]. The material's properties and application areas depend on material morphology and fabricated method. In order to enhance the application range of ZnO materials that respond to both ultraviolet and visible light regions, ZnO nanostructured materials are modified by single doping or co-doping with transition metal ions, noble metal ions, or rare earth metal ions, or composite or hybrid materials to change the shape and reduce the particle size of the materials[7–9,18–31].

In this study, we fabricate ZnO nanostructured materials co-doped with $Co^{2+}$ and $Ni^{2+}$ ions and undoped ZnO materials by low-temperature hydrothermal method and investigate the photocatalytic prop-

erties for methylene blue (MB) dye solution decomposition under visible light radiation.

## MATERIALS AND METHODS

### Chemicals

Zinc acetate dihydrate $(Zn(CH_3COO)_2.2H_2O$ 99%, AR-China); Cobalt(II) sulfate heptahydrate $(CoSO_4.7H_2O$ 99.5%, AR-China) Nickel(II) nitrate hexahydrate $(Ni(NO_3)_2.6H_2O$ 98%, AR-China Sodium hydroxide (NaOH 98%, AR-China); Ethanol (alcohol, $C_2H_5OH$ 99.7%, AR-China), double distilled water.

### Experimental process

A mixed solution of 60 ml include 0.1M solution of $Zn(CH_3COO)_2$ and 0.1M solution of sodium hydroxide was mixed in a volume ratio of 1:1 and was stirred evenly on a magnetic stirrer for 20 min. Next, the calculated salt amount of $CoSO_4.7H_2O$ and $Ni(NO_3)_2.6H_2O$ was added to the above mixed solution with a molar percentage of $Co^{2+}$ ion (1 mol%) and $Ni^{2+}$ ion (2 mol%) (compared to the number of moles of $Zn^{2+}$ in the solution). Continue to stir the above mixed solution evenly for another 20 min. Then, hydrothermally heated at $90^oC$ for 12h. The paste mixture after hydrothermal process was filtered and washed thoroughly with distilled water and absolute alcohol. This clean paste was next dried at $90^oC$ for 24h. The product obtained was a fine ZnO paste powder co-doped with 1 mol% $Co^{2+}$ and 2 mol% $Ni^{2+}$ and was denoted ZnO-1%Co-2%Ni. An undoped ZnO material sample was prepared with the same above process but without the addition of $CoSO_4.7H_2O$ and $Ni(NO_3)_2.6H_2O$ salts, resulting in an undoped ZnO sample, which was denoted ZnO, used in experiments for comparison. Figure 1 wasthe ZnO-1%Co-2%Ni and ZnO paste powder sample after hydrothermal process at $90^oC$ for 12h.

The characterization of $Co^{2+}$, $Ni^{2+}$ co-doped ZnO materials (ZnO-1%Co-2%Ni) was measured by the following methods: X-ray diffraction method (XRD, X'pert Pro), Cu-K$\alpha$ radiation ($\lambda$ = 1.54065 Å), scanning angle $2\theta$ » $25\text{-}75^o$; Scanning electron microscopy, X-ray energy scattering spectroscopy (SEM/ EDX, HITACHI TM4000 Plus); solid UV-Vis absorption/reflectance spectra (Jasco V-750), scanning speed 200 nm/min.

Photocatalytic experiments: Accurately weigh 0.015g of each sample of photocatalysts ZnO-1%Co-2%Ni and ZnO. Next, put each powder sample into a pyrex glass beaker containing 60 mL of MB solution with a concentration of 10 ppm. This reaction dye solution was stirred and left completely dark for 1 hour
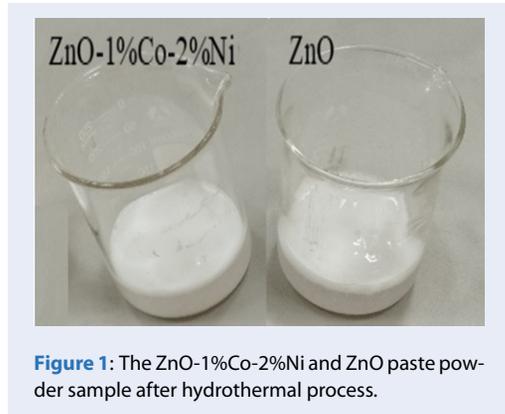
to achieve adsorption and desorption equilibrium. Next, the solution was irradiated under a visible light source (using Osram 220V-250W lamp, Philip brand) at room temperature. At each survey period, took out 2 mL of the solution and measure the absorbance on a UV-Vis photometer system (Agilent 8453) at a max wavelength (664 nm). The remaining content (%) of MB dye after the photocatalytic decomposition process was determined according to the following formula (in which, $C_o$ and $C_t$ were the initial and after a certain irradiation time (t) MB dye solution concentration, respectively).

The remaining content (%) = $(C_t/C_o)$ x100 (1)

## RESULTS AND DISCUSSION

### Structural characterization of materials

The results of the X-ray diffraction spectra of the ZnO-1%Co-2%Ni and ZnO samples were shown in Figure 2. The XRD spectra presented that the ZnO-1%Co-2%Ni and ZnO samples both appear peaks at the diffraction angle site 2q» $31.7°$, $34.3°$, $36.2°$, $47.45°$, $56.6°$, $62.8°$ and $67.25°$ which attributed to the lattice planes of (100), (002), (101), (102), (110), (103) and (112) of ZnO hexagonal wurtzite structure with space group P63mc[8,20]. On the other hand, on the XRD spectra, no other strange peaks were observed, which were attributed to Co or Ni elements or compounds of those elements[19,20,22,31]. So, it could be seen that the ZnO-1%Co-2%Ni and ZnO material samples were hexagonal wurtzite ZnO single-phase, and the $Co^{2+}$ and $Ni^{2+}$ ions had been successfully doped into the ZnO material in the form of replacing the $Zn^{2+}$ ion site. This could also be easily seen because the doped elements (Co and Ni) all had ionic radii that were approximately the same as the radius of $Zn^{2+}$ ion $(r(Zn^{2+})$ = 0.74 Å, $r(Co^{2+})$ = 0.72 Å, $r(Ni^{2+})$ = 0.70 Å)[19,20,22,31].

The average crystallite size of the ZnO-1%Co-2%Ni and ZnO samples was calculated by applying the Scherrer equation [6,7]:

$$D = K\lambda / \lambda \cos\theta \qquad (1)$$

In which, D is the average crystal size; K is a coefficient that depends on the shape of the crystal K = 0.9; $\lambda$ = 1.54056 Å is the diffraction wavelength; $\beta$ is the full width at half maximum (FWHM), $\theta$ is the diffraction angle at the position of the (101) diffraction plane. The calculation results showed that the average crystal sizes of the ZnO-1%Co-2%Ni and ZnO samples were 25.06 nm and 29.48 nm, respectively. Thus, the $1\%Co^{2+}$, $2\%Ni^{2+}$ co-doped ZnO sample had reduced the average crystal size more than the undoped ZnO sample. This further confirms that the $Co^{2+}$ and $Ni^{2+}$ ions had interacted and were doped into the crystal lattice of ZnO.



**Figure 3**: The scanning electron microscope (SEM) of the ZnO-1%Co-2%Ni and ZnO samples
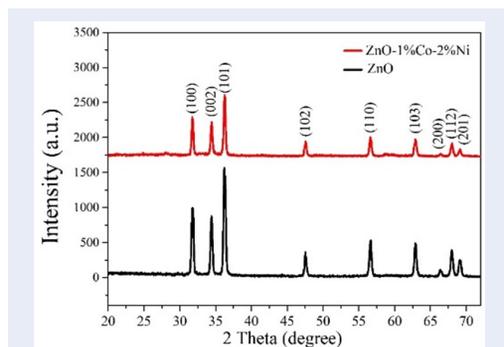


**Figure 2**: The X-ray diffraction spectra (XRD) of ZnO-1%Co-2%Ni and ZnO samples

## Material surface morphology

Figure 3 was a scanning electron microscope (SEM) of ZnO-1%Co-2%Ni and ZnO samples. The SEM image indicated that the surface of the ZnO sample had a thin flake shape. The ZnO-1%Co-2%Ni sample had the form of small particles that were gradually separated from the thin flakes and was distributed relatively uniform on the surface. Thus, the surface state of ZnO-1%Co-2%Ni sample was changed compared to undoped ZnO sample. This showed the possibility of changing the photocatalytic properties of doped ZnO materials compared to undoped ZnO. Figure 4 was the X-ray energy scattering spectra of ZnO-1%Co-2%Ni and ZnO samples.

The EDX spectra of ZnO sample indicated that only the spectral peaks of the two Zn and O elements that made up the ZnO material were observed. In the
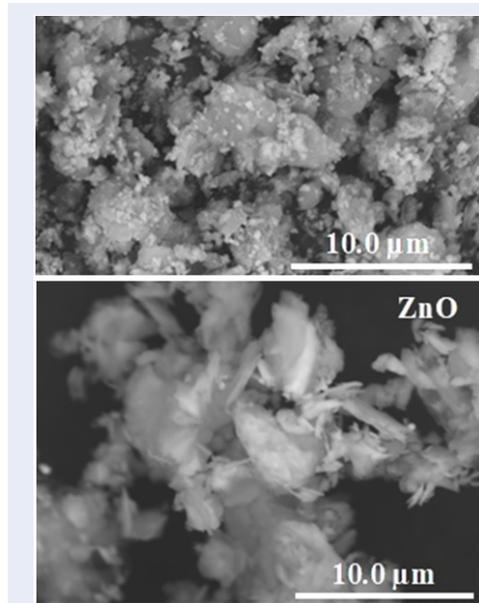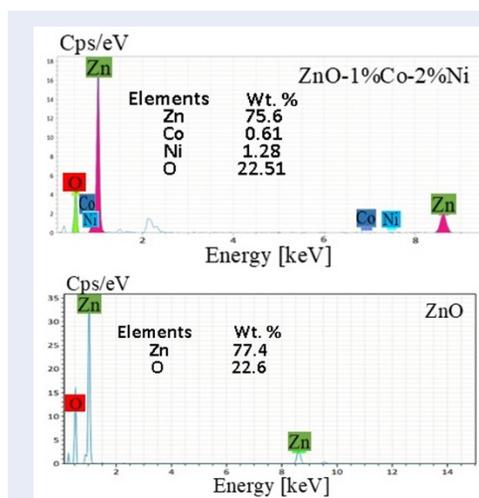


**Figure 4**: The X-ray energy scattering spectra (EDX) of the ZnO-1%Co-2%Ni and ZnO samples

ZnO-1%Co-2%Ni sample, it showed that in addition to the Zn and O elements, there were also spectral peaks with low intensity of the two Co and Ni elements. Thus, it could be seen that the ZnO sample was fabricated in the form of pure wurtzite ZnO phase. The ZnO-1%Co-2%Ni sample was also in the form of pure wurtzite ZnO phase but was doped into the ZnO crystal lattice by two Co and Ni elements.

### UV-vis absorption spectra and function plot d(F(R)h ))/dE with energy h (Kubelka–Munk)

Figure 5 was the Uv-vis spectra of ZnO-1%Co-2%Ni and ZnO samples. On the Uv-vis spectra indicated that ZnO sample had an absorption edge in the ultraviolet region (l ≤ 385nm). The ZnO-1%Co-2%Ni sample had an absorption edge that was broadened and shifted toward visible light region (l » 400nm). It could be seen that ZnO sample would only be capable to achieve applications photoexcitated of light in the ultraviolet region. The ZnO-1%Co-2%Ni sample would provide the possibility to achieve applications photoexcitated of light in the visible region [18].

Applying the Kubelka-Munk (K-M) method to further exploit the optical properties of the material, the Eg value of samples were determined by extrapolation according to the K-M equation [18] as follows.

$$d[\ln(F(R) \times h\nu)]/d(h\nu) \ = \ n/(\ h\nu - Eg) \qquad (3)$$

In which, F(R) was a function of the diffuse reflectance coefficient determined from the diffuse reflectivity coefficient R to F(R)= $(1-R)^2/2R$; $h\nu$ was the photon energy variable; Eg was the optical gap energy. The Eg value of samples were extrapolated from the function plot of d[ln(F(R)h$\nu$)(h$\nu$) vs h$\nu$ energy (Figure 6). The extrapolation results for the optical gap energy values of the ZnO-1%Co-2%Ni and ZnO samples were 3.17 eV and 3.34 eV, respectively. The Eg value of the ZnO-1%Co-2%Ni sample was shown to be smaller than that of the ZnO sample and also smaller than that of bulk ZnO (3.37 eV) [1,2]. Thesse Eg values of the samples were found to be consistent with their solid Uv-vis spectra (Figure 5) This demonstrated the possibility of achieving light-excited optical applications in the visible region of the ZnO sample doped by 1%Co$^{2+}$ and 2%Ni$^{2+}$ ions.

### Investigation of photocatalytic properties

Figure 7a was the plot surveying the MB dye remaining content (%) after photocatalytic decomposition process under visible light exposure time of ZnO-1%Co-2%Ni and ZnO samples.

The plot (Figure 7a) showed that ZnO-1%Co-2%Ni sample had a MB remaining content of 12.38% (corresponding to achieving a photocatalytic efficiency for MB decomposition of 87.62% after 3.5 h of visible light exposure). The ZnO sample almost could not MB decompose, the MB remaining content was 81.85% (corresponding to only achieving a photocatalytic efficiency for MB decomposition of 18.48%). Therefore, it could be said that ZnO-1%Co-2%Ni
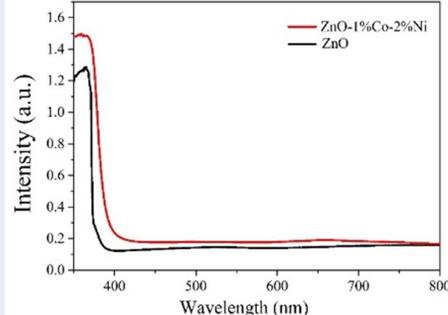


**Figure 5**: The solid Uv-vis absorption spectra of the ZnO-1%Co-2%Ni and ZnO samples
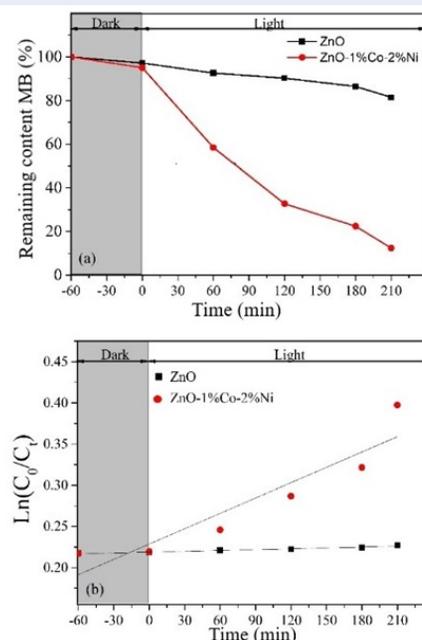


**Figure 7**: a- The MB dye remaining content at irradiation time; b- Kinetic decomposition of MB dye solution through the linear relationship of the plot Ln(C$_o$/C$_t$) vs visible light irradiation time of ZnO-1%Co-2%Ni and ZnO samples

sample has achieved superior properties compared to the undoped ZnO sample, that is, it has allowed to achieve effective photocatalytic decomposition of MB dye solution in the visible light.

The rate constant for the photocatalytic decomposition reaction of MB dye was determined based on the Langmuir-Hinshelwood (L-H) kinetic model [7,21] as follows
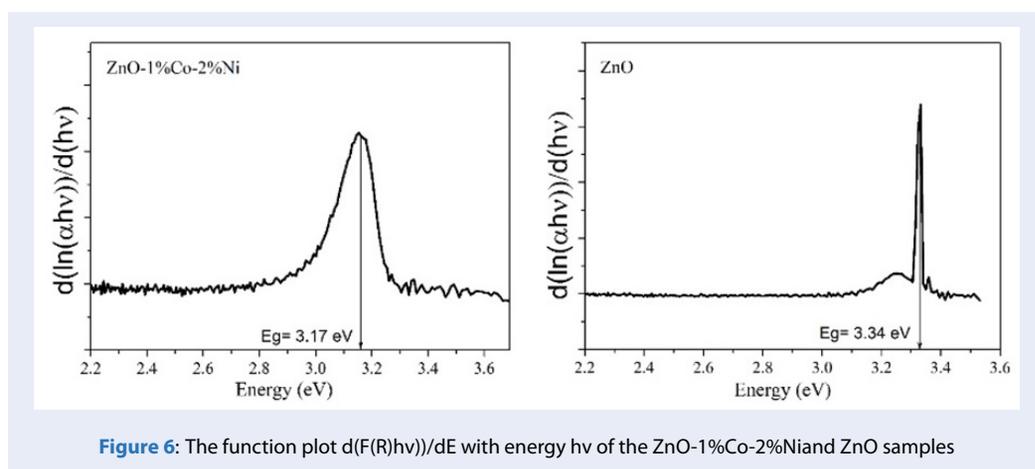
$$\ln(C_o/C_t) \ = \ kt \qquad (4)$$

**Figure 6**: The function plot d(F(R)hv))/dE with energy hv of the ZnO-1%Co-2%Niand ZnO samples

Where $C_o$ and $C_t$ are the initial and concentration of MB at a certain time interval and k is the rate constant. On the L-H kinetic model (Figure 7b) showed that the plot of $\ln(C_o/C_t)$ vs time followed a linear relationship (first order function) with a quite good $R^2$ correlation coefficient ($R^2 \geq 0.92$). The k rate constant of ZnO-1%Co-2%Ni and ZnO samples was determined as 0.0006204 and 0.00003471 $min^{-1}$, respectively. It was found that the k rate constant of ZnO-1%Co-2%Ni sample was many times larger than that of undoped ZnO sample. The rate constant k shows that the larger its value, the faster the rate efficiency for the MB dye decomposition reaction.

## CONCLUSION

Experiments had successfully fabricated ZnO-1%Co-2%Ni and ZnO nanostructured materials at low temperatures. The fabricated samples had a hexagonal wurtzite structure. The ZnO-1%Co-2%Ni sample had reduced the average crystal size more than the undoped ZnO sample. The average crystal sizes of the ZnO-1%Co-2%Ni and ZnO samples were 25.06 and 29.48 nm, respectively. The optical gap energy (calculated according to the K-M method) of ZnO-1%Co-2%Ni sample (3.17 eV) was smaller than that of ZnO sample (3.34 eV). The ZnO-1%Co-2%Ni sample achieved the ability for decompose MB dye solution under visible light. The undoped ZnO sample had almost no effect on decomposing MB under visible light. The MB decomposition rate constant of ZnO-1%Co-2%Ni and ZnO samples followed a first-order kinetic model with good correlation coefficient ($R^2 \geq 0.92$). The rate constant of ZnO-1%Co-2%Ni sample (0.006204 $min^{-1}$) was much larger than that of undoped ZnO sample (0.0003471 $min^{-1}$).

## CONFLICT OF INTEREST

The authors would like to confirm that there is no conflict of interest in publishing the article.

## CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Ta Ngoc Dung: Methodology, Formal analysis, Supervision; Nguyen Thi Tuyet Mai: Investigation, original draft, Formal analysis, Supervision; Huynh Dang Chinh: Methodology, Formal analysis, Supervision.

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# Nghiên cứu chế tạo và khảo sát các đặc tính cấu trúc, tính chất quang và xúc tác quang của vật liệu cấu trúc nano ZnO pha tạp đồng thời Co$^{2+}$, Ni$^{2+}$

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**TÓM TẮT**

Trong nghiên cứu này đã chế tạo thành công vật liệu cấu trúc nano ZnO pha tạp đồng thời Co$^{2+}$, Ni$^{2+}$ (Co,Ni-ZnO NMs) bằng phương pháp thủy nhiệt ở nhiệt độ thấp ở 90⁰C trong 12 giờ. Các ion Co$^{2+}$ và Ni$^{2+}$ được pha tạp vào vật liệu nano ZnO với tỷ lệ theo số mol lần lượt là 1 % và 2 % (được tính toán so với số mol của ion Zn$^{2+}$). Các phương pháp nghiên cứu để xác định các đặc tính cấu trúc, tính chất quang và tính chất xúc tác quang phân hủy chất màu methylene blue (MB) được sử dụng như là XRD, SEM, EDX, UV-vis rắn/ lỏng. Kết quả khảo sát cho thấy, vật liệu chế tạo ở dạng cấu trúc đơn pha wurtzite với kích thước hạt tinh thể nano-mét. Năng lượng khe trống quang được xác định theo phương trình Kubelka–Munk và đạt được cỡ 3,17 eV nhỏ hơn so với ZnO không pha tạp (3,34 eV). Điều này là mong muốn trong nghiên cứu về vật liệu bán dẫn để cải thiện tính ứng dụng của vật liệu kích thích được ánh sáng dịch chuyển về vùng nhìn thấy. Đồng thời kết quả khảo sát cũng cho thấy vật liệu nano ZnO pha tạp đồng thời Co$^{2+}$, Ni$^{2+}$ đạt được hiệu quả xúc tác quang phân hủy chất màu methylene blue (MB) trong vùng ánh sáng nhìn thấy. Như vậy, vật liệu ZnO pha tạp đồng thời các ion Co$^{2+}$ và Ni$^{2+}$ đã đạt được tính ưu việt trong những ứng dụng quang học được kích thích bởi ánh sáng khả kiến (vật liệu ZnO không pha tạp chỉ đạt được ứng dụng quang học trong vùng ánh sáng tử ngoại). Hằng số tốc độ của phản ứng phân hủy quang xúc tác đối với thuốc nhuộm MB đã được xác định theo mô hình động học Langmuir Hinshelwood (L-H). Hằng số tốc độ phân hủy này của các mẫu chế tạo đều tuân theo mô hình động học bậc nhất với hệ số tương quan R$^2$ cao (đạt trên 0,92). Hằng số tốc độ của mẫu Co,Ni-ZnO NMs lớn hơn khoảng 17,8 lần so với mẫu ZnO không pha tạp (đạt lần lượt là 0,006204 và 0,0003471 phút$^{-1}$).

**Từ khoá:** Cấu trúc nano Wurtzite ZnO, ZnO pha tạp đồng thời Co2+, Ni2+, Kubelka–Munk, ánh sáng nhìn thấy

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